Paper No. 5059
CNS WM 2005 Conference, May 8-11, Ottawa

Experience With Remediating Radiostrontium-Contaminated Ground Water and Surface Water with Versions of AECL's CHEMIC^{TM} Process

Shiv Vijayan
Atomic Energy of Canada Limited
Chalk River Laboratories, Chalk River, Ontario, Canada K0J 1J0

ABSTRACT

Numerous approaches have been developed for the remediation of radiostrontium (^{90}Sr) contaminated ground water and surface water. Several strontium-removal technologies have been assessed and applied at AECL's (Atomic Energy of Canada Limited) Chalk River Laboratories. These include simple ion exchange (based on non-selective natural zeolites or selective synthetic inorganic media), and precipitation and filtration with or without ion exchange as a final polishing step. AECL's CHEMIC^{TM} process is based on precipitation-microfiltration and ion-exchange steps.

This paper presents data related to radiostrontium removal performance and other operational experiences including troubleshooting with two round-the-clock, pilot-scale water remediation plants based on AECL's CHEMIC^{TM} process at the Chalk River Laboratories site. These plants began operation in the early 1990s. Through optimization of process chemistry and operation, high values for system capability and system availability factors, and low concentrations of ^{90}Sr in the discharge water approaching drinking water standard can be achieved.

INTRODUCTION

Radiostrontium (^{90}Sr) is a relatively long-lived radionuclide (half-life 29 years) commonly found in many ground water and surface water systems migrating from historic nuclear waste storage sites. The waters also generally contain trace amounts of stable strontium, toxic metals along with alkali-earth metals and iron. The concentrations of toxic metals are in the order of a few mg/L whereas concentrations of radiostrontium are typically a few µg/L or lower. The alkali-earth metals, calcium and magnesium, combined with iron are present in relatively higher concentrations, tens to hundreds of mg/L. The contaminated waters are further complicated in certain instances by the presence of large amounts of electrolytes including metal chlorides and sulphates. The challenges for the remediation of ^{90}Sr-contaminated waters arise from the need to achieve very high removal efficiencies, reduced secondary-waste generation as a result of water remediation and cost effectiveness.

Depending on the methods, the presence of other major cations, anions and organics can aid or impede the contaminant removal efficiencies, and also can contribute to the generation of large volumes of secondary waste from the treatment. The evolution of stringent environmental regulatory limits for such contaminants necessitates the development of efficient and cost-effective treatment methods. These must be developed and implemented in closed-loop configurations with high decontamination factors and minimum secondary-waste generation requiring further treatment before storage/disposal.

One of the challenges for the remediation of ^{90}Sr-contaminated waters arises from the need to achieve very high removal efficiencies from waters with relatively high concentrations of other non-radioactive cations (e.g. calcium and magnesium). Low-cost natural zeolites are non-selective for strontium over other divalent cations, and competition for sorption sites by such ions (notably calcium) results in very limited ^{90}Sr removal before effluent concentrations exceed discharge objectives. This produces large volumes of solid waste. Higher removal efficiencies, and much smaller volumes of solid waste, are obtained with strontium-specific synthetic ion exchangers, but the costs of these innovative sorbents are prohibitive for all but limited small-scale applications, unless the cost of waste disposal is extremely high. In certain applications, non-selective treatment involving bulk chemical precipitation and filtration may be a more viable option.

CHEMIC™ PROCESS

The AECL's CHEMIC™ (CHEmical treatment and MICrofiltration) process emerged through a logical evolution of ideas and experience gained in particular from a cooperative project between AECL and USDOE managed through Argonne National Laboratory [1,2]. In developing a specific water treatment technology for waste and ground waters, the CHEMIC technology evolved to a more generalized mixed-waste (containing radiological and non-radiological species) treatment technology. Refinements to the process chemistry, testing for expanded applications and plant design have continued [3,4,5,6].

The AECL's CHEMIC™ process for ^{90}Sr removal (Figure 1) from surface and ground waters with relatively high calcium and other cations consists of an initial adjustment of the ground/surface water chemistry to convert soluble ionic species to filterable solids. This allows particle size enlargement by precipitation, co-precipitation and adsorption/ion exchange. The suspended particles, consisting of the target species such as radiostrontium and other metals, are removed by the use of cross-flow microfiltration and by gravity settling. The majority of the process filtrate, which meets the target water quality, is discharged either directly after pH adjustment or, if necessary, through a set of fixed-bed natural zeolite ion-exchange columns to meet the required discharge water quality. The concentrated residual waste, which contains >99% of the ^{90}Sr inventory, is immobilized in a cement binder to produce a stable waste form for long-term storage and final disposal.

RADIOSTRONTIUM REMOVAL FROM GROUND WATERS AT AECL'S CRL SITE

Water Characteristics

Experiences were gained in radiostrontium-removal by treating two types of ^{90}Sr-contaminated waters at the AECL's CRL site. The first stream (SB) represents a combination of surface and ground water containing relatively high levels of calcium (25 mg/L), while the other ground water stream (CP) contains low levels of calcium (2 mg/L). The approximate composition of each stream is listed in Table 1. The actual concentrations of the dissolved species vary depending on weather and specifically on the amount of surface water that enters the water table from rain or melting snow .

Table 1: Stream Characteristics

Species	Concentration SB (Ground and Surafce Waters)	 CP (Ground Water)
Strontium (stable Sr) (mg/L) Strontium-90 (Bq/L) Strontium-90 (mg/L)	0.4 2500 5×10^{-7}	0.03 1000 1.9×10^{-7}
Calcium (mg/L)	25 - 50	2 - 5
Iron (mg/L)	10	0.05
Magnesium (mg/L)	7	0.7
Sodium (mg/L)	35	12
Bicarbonate/carbonate (mg/L)	110	---
Conductivity (µS/cm)	500	60
Solution pH	6.5	6.0

Note: Although the concentrations for these species will have large variability with time, the values reported represent an average determined from the analysis of a representative number of pooled ground water samples taken during a continuous run. Specific activity of ^{90}Sr is 5.09 x10^{12} Bq/g.

Process Chemistry and Operation

Versions of the CHEMIC process for the removal of ^{90}Sr from different waters were implemented in the SB water (~7.6 L/min or 2 US gal/min throughput) remediation facility, and the CP water (15 L/min or ~4 US gal/min throughput) remediation facility at AECL's Chalk River Laboratories. Round-the-clock operation of the two treatment facilities began in 1994. Treatment of the SB water uses a modified lime-soda treatment step at room temperature (~20-25^{o}C) by electrical heating of the water prior to conditioning at a pH value in the range of 10.5 to 11.0 with sodium hydroxide to remove Sr, ^{90}Sr, Ca and Fe as suspended particles (precipitates and cation-sorbed particulates) by cross-flow microfiltration. The filtrate stream after filtration is neutralized with carbon dioxide and treated through clinoptilolite sorption columns.

Because the CP water had much lower cation and anion concentrations than originally anticipated , a version of the CHEMIC flow sheet involving precipitation and vacuum rotary-drum filtration, and zeolite-column sorption was discontinued in 1998, and replaced with a simpler treatment based on sorption of ^{90}Sr on clinoptilolite, a natural zeolite. Treatment of the CP water uses cartridge prefiltration and sorption by clinoptilolite columns at the prevailing groundwater temperature (6-10^{o}C). There is no pH adjustment of the water during treatment.

The treatment system was designed to operate with minimum operator intervention. The process is controlled from panels on the individual process equipment. Each process equipment module has its own safety features to ensure compliant operation. There are interface controls between the collection well and the feed conditioning systems, and between the feed conditioning systems and the microfiltration unit. The four microfilters used in the treatment system are hollow fibre, polypropylene membranes with a total surface area of 4 m^2 and average pore-size of 0.2 µm diameter.

The SB water treatment starts from the collection well that collects and pumps the contaminated water to the feed tank by means of a sump pump. The water is then passed through conditioning tanks where the addition of chemicals takes place. The suspension from the conditioning tank is then fed to a cross-flow microfiltration unit to achieve solid-liquid separation.

The filtrate from the microfiltration unit is stored in the neutralization tank where the solution pH is monitored and adjusted. The filtrate is then pumped through a polishing system equipped with two sets of ion-exchange columns arranged in parallel. The treated water is temporarily stored in a holding tank and samples are taken from the tank for chemical analyses. The treated water is discharged if its quality meets the discharge target; otherwise it is recycled for more treatment. A backwash cycle and a sulphuric acid-wash cycle are also included in the treatment system to increase the process efficiency and the life span of the microfilters. The concentrated slurry resulting from the backwash cycle, which is employed for microfilter recovery, and any settled solids from the feed tank are then solidified in a cement matrix.

The CP water treatment starts from four groundwater wells that collect and pump the contaminated ground waters via a set of filters, housed in a pump house, to the feed tank. The rates of pumping of the individual wells are controlled with respect to water level in a reference well. This mode of pumping minimizes any well overdraws. The ground water is then passed through 2 or 3 sets of zeolite columns (~0.016-m dia. x 1-m high) arranged in a parallel configuration. The treated water is discharged down-gradient of the contaminated plume.

RADIOSTRONTIUM REMOVAL PERFORMANCE

Temperature Effect

Field tests were conducted at four different temperature ranges; one of which was not controlled at the prevailing temperature of the ground water being treated. Filtrate samples after precipitation and microfiltration were analyzed for ^{90}Sr and Ca. Tests were performed over a range of temperatures (5.5 to 26.5^{o}C). The results are given in Table 2.

Table 2: Temperature Effect on Treated Water Quality Using SB Water

Feed Water Temperature Range (°C)	Number of Samples Analyzed	Concentration in Feed Water		Concentration in Filtrate (Treated Water) after Precipitation and Microfiltration	
		^{90}Sr (Bq/L)	Calcium (mg/L)	^{90}Sr (Bq/L)	Calcium (mg/L)
5.5-10 (no heating)	7	1850-2057 (ave. 1970)	25.6-31.2 (ave. 29.0)	302-508 (ave. 427)	4.2-9.2 (ave. 5.5)
15-17 (heating controlled at 16°C)	8	1906-2020 (ave. 2000)	18.6-32.0 (ave. 27.5)	49-104 (ave. 74.6)	1.6-3.6 (ave. 2.7)
20-22 (heating controlled at 21°C)	6	1750-2320 (ave. 2090)	31.4-38.7 (ave. 36.2)	26-67 (ave. 41.6)	1.2-3.0 (ave. 2.2)
24.5-26.5 (heating controlled at 25°C)	6	2218-2777 (ave. 2494)	31.6-35.7 (ave. 33.6)	27-35 (ave. 30.3)	1.1-1.8 (ave. 1.5)

Because of the favourable ^{90}Sr and Ca removal efficiencies as a result of decreased solubility of precipitated carbonates of the metals around 20°C to 25°C, the room temperature regime was implemented as the operating temperature for the treatment of the SB water.

Removal Behaviour of Calcium, Stable Strontium and Strontium-90

The operational data obtained from the SB and CP remediation facilities between 2003 September and November are summarized in Table 3. Within the uncertainties associated with sampling and analysis, the results given in Table 3 do not reveal a simple relationship among the removal performance of stable Sr, ^{90}Sr and Ca in the untreated and treated waters. This may be due to the leaching of stable strontium and calcium from the natural zeolite during the final treatment stage, which would not contribute any ^{90}Sr to the treated water. However, higher calcium levels in the untreated water correspond to higher stable strontium and ^{90}Sr levels, reflecting consistent water leaching characteristics of the cations from the contaminated soil. For CHEMIC process, lower calcium levels in the water appear to produce lower levels of stable Sr and ^{90}Sr in the treated water, illustrating generally consistent removal behaviour during precipitation and sorption, which is expected among these cations because of their similar chemical properties. The results also suggest that the relatively higher levels (in molar concentration) of stable Sr and Ca present in the waters, as compared to ^{90}Sr will limit the effectiveness of the treatment process for ^{90}Sr removal and the waste volume reduction factor (VRF), which is defined as the volume of water treated divided by volume of stabilized secondary waste produced as a result of treatment.

Table 3: Some Removal Data for Ca, Stable Sr and ^{90}Sr

SB Water			CP Water		
Ca (mg/L)	Sr (µg/L)	^{90}Sr^{1} (Bq/L)	Ca (mg/L)	Sr (µg/L)	^{90}Sr^{1} (Bq/L)
Untreated Water					
49±3	420±80	3000±90	3.4±0.2	33±7	2200±60
42±3	360±70	2800±100	4.2±0.2	32±6	2200±60
41±2	340±70	2700±100	4.9±0.3	45±9	2600±80
41±2	330±70	2500±100	3.9±0.2	30±6	1300±40
Treated Water					
4.0±0.2	190±40	3.5±0.3	3.0±0.2	26±6	5.2±0.3
4.5±0.3	190±40	10±1	2.6±0.2	21±4	6.5±0.3
4.4±0.2	180±40	11±1	2.0±0.1	21±4	4.8±0.3
3.9±0.2	170±40	7.5±0.3	2.4±0.1	14±3	13±1

Note: 1) The quoted uncertainties are at 1s level.

^{90}Sr Removal Performance in Routine Treatment of SB and CP Ground Waters

Since 1994, ground water remediation of SB and CP ^{90}Sr-contaminated waters has resulted in the successful treatment of over 50 million litres (13.2 million US gallons) and reduced ^{90}Sr in the discharge by a factor of 100 to 1000. The overall waste VRF has been in the range of 600 to 3000. A summary of the last five years of performance data is given in Table 4 and Figure 2 for the SB water and in Table 5 and Figure 3 for the CP water.

Table 4: ^{90}Sr Removal Performance of SB Water on an Annual basis

Year	Average ^{90}Sr in Untreated Water (Bq/L)	Average ^{90}Sr in Treated Water (Bq/L)	Volume of Treated Water (L)	Secondary Waste Volume^{1} (No. of 200-L Drums)	Average ^{90}Sr Removal Efficiency (%)	System Availability^{2} (%)	System Capability^{3} (%)	VRF^{4}
2000	2600±100	60±2	3,030,000	25	98±5	92	90	606
2001	3100±100	12±1	3,027,184	22	100±5	93	68	688
2002	2700±100	17±1	2,790,000	14	99±5	91	86	996
2003	2600±100	21±1	3,120,000	9	99±5	94	92	1733
2004	2500±100	21±1	3,184,332	10	99±6	91	96	1592

Notes: 1: Volume of secondary waste stabilized in cement which would meet the waste-form guideline in ref. [7].
2: System Availability is the percent of time the system was available to treat water in a year.
3: System Capability is the percent of actual volume of water treated annually as compared to the volume that can be treated.
4: Volume Reduction Factor, VRF, is the ratio of the volume of water treated to the volume of secondary waste (stabilized in cement) produced.

Table 5: Strontium-90 Removal Performance of CP Water on an Annual basis

Year	Average ^{90}Sr in Untreated Water (Bq/L)	Average ^{90}Sr in Treated Water (Bq/L)	Volume of Treated Water (L)	Secondary Waste Volume[1] (No. of 200-L Drums)	Average ^{90}Sr Removal Efficiency (%)	System Availability[2] (%)	System Capability[3] (%)	VRF[4]
2000	1200±40	50±3	3,800,000	9	96±5			2111
2001	1300±40	11±1	4,070,000	7	99±4			2907
2002	1600±50	37±2	4,550,000	8	98±4	96	140	2844
2003	1700±50	5±1	3,840,000	5	100±4	97	100	3840
2004	900±30	6±1	4,570,480	3	99±5	95	117	7617

Notes: 1: Volume of secondary waste stabilized in cement which would meet the waste-form guideline in ref. [7].

2: System Availability is the percent of time the system was available to treat water in a year.

3: System Capability is the percent of actual volume of water treated annually as compared to the volume that can be treated.

4: Volume Reduction Factor, VRF, is the ratio of the volume of water treated to the volume of secondary waste (stabilized in cement) produced.

Waste Stabilization

The recovered ^{90}Sr in secondary waste is stabilized in cement and drummed. Radiostrontium (^{90}Sr) inventories in the drums are estimated based on the operational data. The waste form meets or exceeds the United States Nuclear Regulatory Commission guidelines [7] for both the leachability index and mechanical strength to permit long-term storage or final disposal in engineered low-level radioactive waste disposal facilities. The final treated discharge water has a solution pH in the range of 7 to 8 and the total dissolved solids is generally between 500 and 600 mg/L. The treatment plant can be monitored regularly and remotely using personal computers connected through modems. The plants continue to operate at an average of 90% of the time and treat 80 to 100% of the design treatment capacity.

Technology Attributes/Issues

The AECL CHEMIC^{TM} technology performs reliably over a range of operating conditions for the removal of radionuclides and heavy metal contaminants. The process limitations include: a) processing temperature, b) suspended solids concentration after chemical treatment of the contaminated water, c) radioactivity of concentrated streams in the process, and d) ground water chemistry.

The technology is designed to operate at room temperature (20 to 25°C) although its performance should be reliable over 7 to 40°C. Processing outside the recommended temperature range can adversely reduce overall contaminant removal efficiency. Furthermore, suitable design specification of components including pumps, sensors and materials will be needed to operate at higher than 40°C.

The maximum recommended concentration of suspended solids after chemical precipitation and sorption of contaminants is 0.2 wt.%. A higher concentration of suspended solids reduces the overall waste volume reduction that can be obtained using this technology and also can reduce the microfilter life. The technology would require pre-filtration upstream of the microfiltration unit if the feed water contains particulates greater than 100 µm diameter.

Another limitation arises from safety considerations to deal with radiation fields around the microfiltration system, dewatering system, and secondary waste handling area when the technology is utilized to treat a wastewater, which contains high concentrations of beta- and gamma-emitting radionuclides. However, with adequate shielding installed around the equipment and with proper operating procedures, one can minimize the radiation exposure to the operator.

At the outset, it is important to have the feed water thoroughly analyzed to be in a position to understand and predict the chemistry (type of contaminants, impurities, etc.) in order to design the optimum treatment chemistry and to select the appropriate materials of construction. For example, the process presently uses a polypropylene hollow-fibre microfilter, which is incompatible with high concentrations of organic solvents or free chlorine. The performance of the process depends heavily on the water chemistry. If the composition of the feed water changes significantly, the chemistry of the process should be re-evaluated to ensure and maintain high contaminant removal efficiency. For example, for ^{90}Sr removal, the precipitant dosing levels should be increased when the concentration of ^{90}Sr or its competing species, calcium, increases significantly in the feed water. The presence of appreciable amounts of metal complexing agents in the water can seriously affect (reduce) the contaminant removal efficiency. The type of precipitant and the precipitation-sorption pH can be changed once a priori evaluation of the water to be treated has been made. If significant fractions of the contaminants are complexed by natural humic substances, then the current technology would not provide desirable removal efficiencies for contaminants.

Quality Control

Influent and effluent are sampled and analyzed for ^{90}Sr routinely. Occasionally, samples of the process streams (e.g. filtrate from the mircofiltration unit) are also analyzed for ^{90}Sr and calcium. Influent from the feed water tank and effluent from the treated water tank are collected in sample bottles continuously using metering pumps. Each week, a representative number of pooled samples are analyzed for ^{90}Sr. In addition continuous monitoring of pH and electrical conductivity of the treated water are performed using in-line sensors.

The ^{90}Sr concentration in liquid samples is determined by sample preparation through chemical treatment-gravimetry, or by selective ion-exchange separation, followed by liquid scintillation counting. Other species such as iron, calcium, manganese, magnesium, sodium and bicarbonate are also analyzed non-routinely on an as-needed basis to evaluate the process.

CONCLUSIONS

On the basis of radiostrontium removal experiences with low and high calcium contents surface and ground waters using versions of the CHEMIC process, the following conclusions can be drawn:

- Experience with the application of the CHEMIC process, involving chemical precipitation and microfiltration and a final polishing step with natural zeolites such as clinoptilolite sorption shows that this approach can readily remove >99 % of the ^{90}Sr yielding very low concentrations of ^{90}Sr in the treated water from a high calcium content ground water.
- Because most of calcium is removed by precipitation in the full CHEMIC process, there is no apparent advantage for using high-cost sorbents, such as crystalline silicotitanate or SrTreat, over natural zeolite sorbents in the polishing system.
- For low calcium ground waters, the application of non-selective, natural zeolites, for the removal of radiostrontium is the preferred approach.

ACKNOWLEDGEMENTS

This paper is dedicated to the late Dr. Don Cameron of AECL, whose vision and encouragement resulted in the development, demonstration and implementation of the CHEMIC process at Chalk River Laboratories. Thanks are also due to several colleagues at AECL, in particular, L.P. Buckley, D. Champ, B. Lange, C.F. Wong, S. Daughney, R. Karivelil, M. Heming, S. Bokwa, M. Beale, P. Burke, E. Williams, D. Ezarin, D. Buchanan, S. Rousseau, C. Taylor, R. Rao, S. Cotnam, L. Moschuck, D. Killey, D. Lee, K. Moore and S. Burdan, who have contributed at various stages either directly or indirectly to the development and continued application of the process.

REFERENCES

1. United States Department of Energy, “ A Cooperative Project, A process for contaminant removal and waste volume reduction to remediate groundwater containing certain radionuclides, toxic metals and organics”, between Atomic Energy of Canada Limited and U.S. Department of Energy, Argonne National Laboratory Contract No. 02112415 (1990).

2. S. Vijayan, C.F. Wong and L.P. Buckley, “Waste Treatment Process for Removal of Contaminants from Aqueous, Mixed-Waste Solutions using Sequential Chemical Treatment and Cross Flow Microfiltration followed by Dewatering”, U.S. Patent 5,366,634; Canadian Patent CA2094103 (1994).

3. S. Vijayan and C.F. Wong, “A Generalized Process for Treating Mixed Radioactive and Metal Contaminants from Groundwaters and Soil Leachates”, Proc. of the Third Biennial Mixed Waste Symp., Baltimore, Maryland, August 7-10; Edrs. A.A. Moghissi, B.R. Love and R.K. Blauvelt, Cognizant Communication Corp., New York, pp. 10.6.1-10.6.15 (1995).

4. S. Vijayan and L.P. Buckley, “Volume Reduction of Wastewaters Containing ^{90}Sr, ^{137}Cs and ^{60}Co Based on AECL CHEMIC^{TM} Technology”, Proc. International Symposium on Radiation Safety Management, ISRSM’97, Korea Electric Power Research Institute/Korea Nuclear Society, November 6-7, Taejon, Korea, pp. 168-177 (1997).

5. S. Vijayan and C.F. Wong, “Uptake of Radiostrontium from Aqueous Solutions by Biomass and Natural Zeolites: Implications in the Treatment of Contaminated Waters by AECL’s

CHEMIC^{TM} Process”, Proc. Waste Management WM’01 Conference, Feb.25-Mar.01, Tucson, Arizona (2001).

6. S. Rousseau and S. Vijayan, “Technology Perspectives on the Removal of Radiostrontium from Large Volumes of Groundwater”, Proc. of the Symposium on Waste Management, Tucson, Arizona (2004).

7. United States Nuclear Regulatory Commission, Low-Level Waste Management Branch, Division of Low-Level Waste Management and Decommissioning, "Technical Position on Waste Form", United States Nuclear Regulatory Commission, January, 1991.

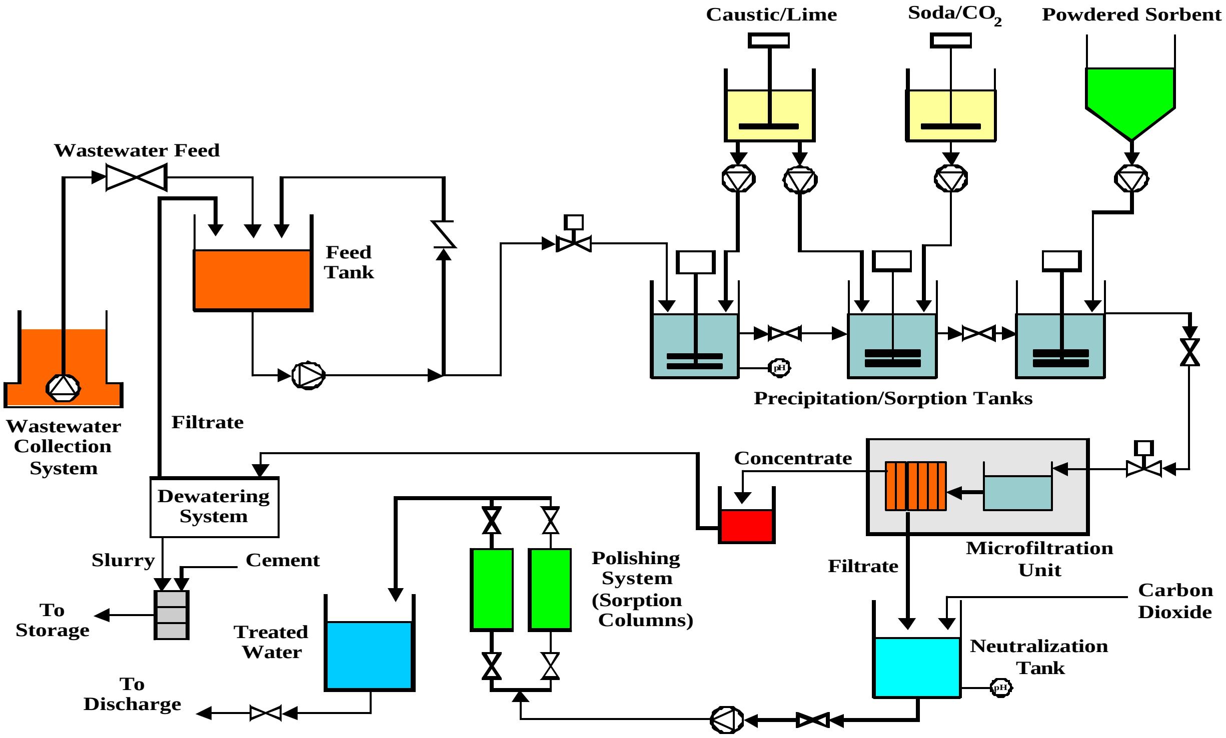

Figure 1: A general CHEMIC flow sheet

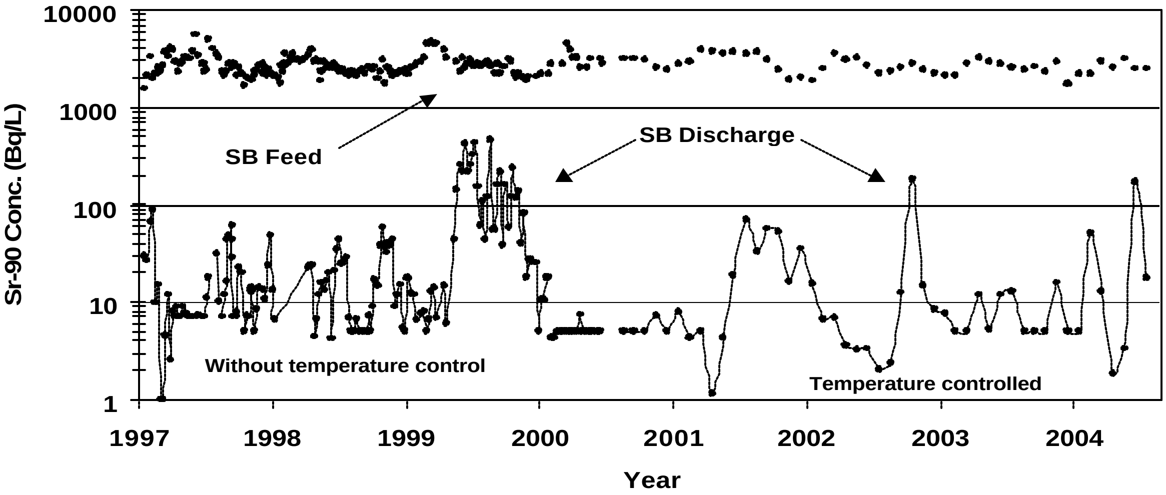

Figure 2: Strontium-90 Removal Performance during 2000-2004
Based on Treatment of SB Surface Water and Groundwater by CHEMIC Process
Involving Precipitation, Microfiltration and Sorption with a Natural Zeolite, Clinoptilolite

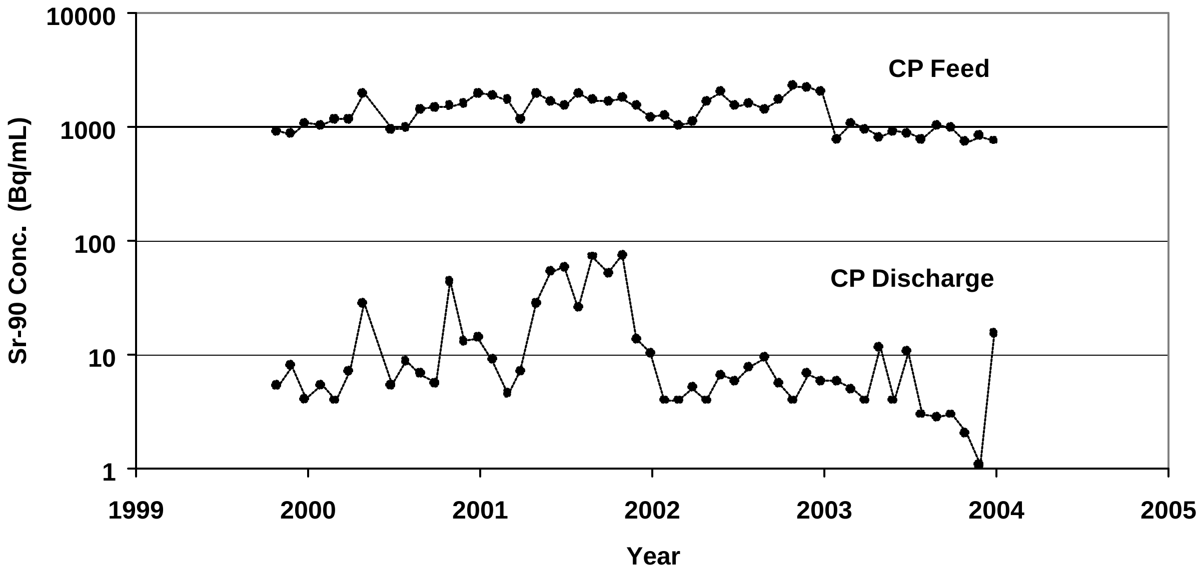

Figure 3: Strontium-90 Removal Performance during 2000-2004 Based on Treatment of CP Groundwater by a Simplified CHEMIC Process Involving Direct Sorption with a Natural Zeolite, Clinoptilolite